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STRETCHABLE LAMINATES

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[There are no amendments to this patent.]

Claims

1. Stretchable laminates are composed of (a) thermoplastic rubber layers composed of 10-150 parts by weight ethylene copolymers and 100 parts by weight hydrogenated block copolymers obtained by hydrogenation of block copolymers composed of polymer block A having at least one aromatic vinyl compound as the main constituent and polymer block B having at least one conjugated diene compound as the main constituent, and (b) nonwoven fabric layers.
2. Stretchable laminates described in Claim 1, characterized in that the hydrogenated block copolymers are styrene-ethylene/butylene-styrene block copolymer.
3. Stretchable laminates described in Claim 1, characterized in that the fibers which constitute the nonwoven fabrics are oriented parallelly in the warp direction.
4. Stretchable laminates described in Claim 1, characterized in that the fibers which constitute the nonwoven fabrics are oriented randomly only in the warp direction.
5. Stretchable laminates described in Claim 1, characterized in that the thermoplastic rubber layer (R) and the nonwoven fabric layer (T) are laminated in ways such as (R)/(T), (R)/(T)/(R), or (T)/(R)/(T).
6. Stretchable laminates described in Claim 1, characterized in that they are manufactured using the T-die chilled roll method.

Detailed explanation of the invention

Industrial application field

The present invention pertains to stretchable laminates made of thermoplastic rubber layers and nonwoven fabric layers.

More precisely it pertains to laminates which can be heat-sealed at low temperature and have excellent mechanical properties, low temperature resistance, and stretchability, and which are suitable as base materials for clothing, bandages, adhesive plasters, diaper covers, packing materials, industrial materials, etc.

Prior art

Heretofore nonwoven fabrics have been used in linings for clothing, medical gauzes, gowns, sheets, masks, top sheets of disposable diapers, diaper linings, cosmetic gauzes, steamed towels, filters, tapes for electric wire, agricultural heat insulators, light-shielding frost-protecting

materials, covering material for tunnel-shaped greenhouse vegetable cultivation, draining materials, soft ground stabilizers, roofing materials, primary packing materials for tufted carpets, ground fabrics for vinyl chloride floor materials, ground fabrics for lasers, artificial leather, artificial suede, liners for floppy disks, various kinds of packaging materials, printing base materials such as labels, etc. However, the nonwoven fabrics which are used in the above-mentioned applications are manufactured by forming sheet-like fiber aggregates (webs), followed by joining the fibers in the webs as in knitted and woven fabrics, therefore there are many fixed points and they are almost not stretchable, thus their uses are limited. Accordingly, stretchable nonwoven fabrics are also in demand and thus heretofore various proposals have been made. For example, nonwoven fabrics using elastic fibers made of polyurethane (Japanese Kokoku Patent Nos. Sho 43[1968]-26592 and Sho 44[1969]-215085), nonwoven fabrics using rubber elastic diene copolymer fibers (Japanese Kokai Patent Application No. Sho 48[1973]-185979), nonwoven fabrics using polyester elastomer fibers (Japanese Kokai Patent Application No. Sho 57[1982]-82552), nonwoven fabrics made by adhering webs composed of crimped acrylic fibers with microporous polyurethane (Japanese Kokai Patent Application No. Sho 53[1978]-139873), nonwoven fabrics comprising silicone fibers self-adhered at the intersection of the fibers (Japanese Kokai Patent Application No. Sho 62[1987]-133163), etc., have been proposed. However, instead of using unstretchable fibers for constituting the nonwoven fabrics, stretchable fibers such as polyurethane, diene copolymer, crimped acrylic fibers, silicone fibers, etc., are used but they are expensive and their physical properties are also different.

Nonwoven fabrics are prepared by joining webs made of fine fibers, so that they have excellent air permeability, but they have almost no waterproof property, dust prevention property, gas barrier property, or bacteria barrier property and their uses are limited.

Problems to be solved by the invention

The object of the present invention is to provide a new material with excellent properties by utilizing the low price and excellent properties of nonwoven fabrics to which excellent properties which nonwoven fabrics alone do not possess are imparted; that is, to provide laminate films having stretchable property, waterproof property, dust-preventing property, gas barrier property, bacteria barrier property, softness, heat sealability, etc.

Means to solve the problems

The present inventors tried to manufacture stretchable nonwoven fabrics by pasting rubber elastic films to webs having irregular fiber orientation. The rubber elastic films were stretchable, but when the webs of the nonwoven fabric were fixed, the fibers constituting the

nonwoven fabrics became fixed at many points so the fibers existed both in the vertical and horizontal directions (i.e., there were both warp and filling) thus they were fixed just as knitted and woven fabrics, and therefore stretchability could not be manifested. To solve the problems, the structure of nonwoven fabrics was changed from the traditional one to a specific one, and by using nonwoven fabrics having the specific structure, it was found that even when the whole nonwoven fabric was fixed by the rubber elastic film, it was able to manifest stretchability. Moreover when traditionally known polyurethanes, polyesters, polybutadienes, silicones, styrene-butadiene copolymers, natural rubber, etc., were used to prepare rubber elastic films, the film formability was very poor, the productivity was very poor and the weather resistance, color tone, odor, etc., of the thus prepared rubber elastic films were inferior. Thus to solve the problems various materials were tested and as a result it was found that when thermoplastic rubber made of specific hydrogenated block copolymers and ethylene copolymers were used, the problems were solved, and thereby the present invention was completed.

That is, the present invention is:

- (1) Stretchable laminates which are composed of (a) thermoplastic rubber layers composed of 10-150 parts by weight ethylene copolymers and 100 parts by weight hydrogenated block copolymers obtained by hydrogenation of block copolymers composed of polymer block A having at least one aromatic vinyl compound as the main constituent and polymer block B having at least one conjugated diene compound as the main constituent, and (b) nonwoven fabric layers.
- (2) The above-mentioned stretchable laminates are characterized in that the hydrogenated block copolymers are styrene-ethylene/butylene-styrene block copolymer.
- (3) The above-mentioned stretchable laminates are characterized in that the fibers which constitute the nonwoven fabrics are oriented parallel in the warp direction.
- (4) The above-mentioned stretchable laminates are characterized in that the fibers which constitute the nonwoven fabrics are oriented randomly only in the warp direction.
- (5) The above-mentioned stretchable laminates are characterized in that the thermoplastic rubber layer (R) and the nonwoven fabric layer (T) are laminated in ways such as (R)/(T), (R)/(T)/(R), or (T)/(R)/(T).
- (6). The above-mentioned stretchable laminates are characterized in that they are manufactured using the T-die chilled roll method.

In the present invention the hydrogenated block copolymer can be obtained by hydrogenating a block copolymer composed of a polymer block A having at least one aromatic vinyl compound as its main constituent and a polymer block B having at least one conjugated diene compound as its main constituent. For example, it can be obtained by hydrogenation of a block copolymer of aromatic vinyl compound having the structure of A-B, A-B-A, B-A-B-A, (A-B)-Si, (B-A-B)-Si, etc.-conjugated diene compound.

In the hydrogenated block copolymer, the aromatic vinyl compound is approximately 60 wt % or less, preferably 45 wt % or less. When it is greater than 60 wt % the hydrogenated block copolymer has no elasticity, thus stretchable laminates of the present invention cannot be manufactured.

In the hydrogenated block copolymer, when the aromatic vinyl compound is 15% or less, the small aggregates (domains) whose glass transition point (T_g) is higher than room temperature become few, the nodes of the rubber phase disappear and rubber elasticity cannot be manifested, which is undesirable.

In the hydrogenated block copolymer, the conjugated diene compound is 40-85 wt %, preferably 55-75 wt %. When it is outside this range the rubber elasticity cannot be manifested.

Further referring to the block structure, the polymer block A having an aromatic vinyl compound as its main constituent has the structure of an aromatic vinyl compound polymer block or a copolymer block structure of a hydrogenated conjugated diene and an aromatic vinyl compound with greater than 50 wt %, preferably at least 70 wt % aromatic vinyl compound, and furthermore the polymer block B with a hydrogenated diene compound as its main constituent has the structure of a hydrogenated conjugated diene polymer block or the structure of a copolymer block of an aromatic vinyl compound and greater than 50 wt %, preferably at least 70 wt % hydrogenated conjugated diene.

In the polymer block A with an aromatic vinyl compound as its main constituent and the polymer block B with a hydrogenated diene compound as its main constituent, the distribution of the aromatic vinyl compound or the hydrogenated conjugated diene compound in the molecular chain in their respective polymer blocks can be random, tapered (the monomer constituent along the molecular chain increases or decreases), partially blocked, or any combination of these, and when there are at least two polymer blocks with an aromatic vinyl compound as their main constituent and at least two polymer blocks with a hydrogenated diene as their main constituent, each polymer block may have either identical or different structures.

Examples of aromatic vinyl compounds which constitute the hydrogenated block copolymer include styrene, α -methylstyrene, vinyltoluene, p-tert-butylstyrene, etc., one or more of them can be selected, and above all, styrene is preferable.

Examples of nonhydrogenated conjugated diene compound which can be used for preparing the hydrogenated conjugated diene compound include butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, etc., one or more of them can be selected, and above all, butadiene, isoprene and their combination is preferable. We can freely select the polymer block with a nonhydrogenated diene compound as its main constituent and the microstructure of the block. For example in polybutadiene block, 1,2-microstructure is 20-50%, preferably 25-45%.

The number-average molecular weight of the hydrogenated block copolymer with the above-mentioned structure used in the present invention is 5000-1,000,000, preferably 30,000-200,000. If it is less than 5000 the film strength becomes weak, which is undesirable, whereas if it is greater than 1,000,000 the formation of films is impossible, which is also undesirable.

The molecular structure of the hydrogenated block copolymer can be linear, branched, radial, or an arbitrary combination thereof.

Any method for manufacturing these block copolymers may be used as long as they have the above-mentioned structure.

For example, using the method described in Japanese Kokoku Patent No. Sho 40[1965]-23798, lithium catalysts are used to synthesize aromatic vinyl compound-conjugated diene compound copolymers in inert solvents, then using the method described in, for example, Japanese Kokoku Patent Nos. Sho 42[1967]-8704, Sho 43[1968]-6636, Sho 45[1970]-20504, Sho 46[1971]-20814, and Sho 48[1973]-3555, especially preferably using the method described in Japanese Kokai Patent Application Nos. Sho 59[1974]-133203 and Sho 60[1985]-79005, they can be synthesized in inert solvents in the presence of hydrogenation catalysts.

Examples of commercially available products include Tuftec (Asahi Chemical Industry Co., Ltd.), Kraton [transliteration] G (Shell Kagaku K.K.), etc. It is preferably to use these.

In the present invention, ethylene copolymers include ethylene-acrylic acid ester copolymer, ethylene-vinyl ester copolymer, metal ion-containing ethylene copolymers, etc.

The ethylene-acrylic acid ester copolymers are prepared by copolymerization of ethylene with a monomer selected from the group consisting of methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, pentyl acrylate, hexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, pentyl methacrylate, hexyl methacrylate, etc.

The ethylene-vinyl ester copolymers are prepared by copolymerization of ethylene with a monomer selected from the group consisting of vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate, etc.

Metal ion-containing ethylene copolymers are ionic bond-containing ethylene copolymers which can be prepared by substituting the hydrogen atoms of the carboxylic group of the ethylene-methacrylic acid copolymer, ethylene-acrylic acid copolymer or ethylene-itaconic acid copolymer, etc., with metallic ions such as sodium, potassium, calcium, magnesium, aluminum, etc., and they are on the market with the trade name of Surlyn [transliteration].

One or a mixture of two or more of the ethylene copolymers used in the present invention may be used.

For the improvement of necking and drawdown properties in extrusion lamination, improvement of blocking, and other purposes, a small amount of low-density polyethylene prepared by high-pressure process, linear low-density polyethylene, polypropylene, etc., may be mixed and used.

The comonomer content in the ethylene copolymer in the present invention is 5-40 wt %, preferably 15-25 wt %.

If it is less than 5 wt % the adhesion to the nonwoven fabrics is poor, whereas if it is greater than 40 wt % the extrusion lamination property, blocking, heat resistance, etc., become poor.

The melt index of the ethylene copolymers used in the present invention is 1-150 g/10 min, preferably 3-60 g/10 min. If it is less than 1 g/10 min the extrusion lamination becomes difficult and the adhesive property becomes poor, whereas if it is greater than 150 g/10 min drawdown occurs and it becomes impossible to process.

As for the ethylene copolymer used in the present invention, the compatibility with hydrogenated block copolymer, workability in the T-die chilled roll process, heat resistance, film formability, adhesive property, etc., of ethylene-ethyl acrylate copolymer are especially excellent.

In the present invention, a resin composition, which is prepared by adding 10-150 parts by weight ethylene copolymer to 100 parts by weight hydrogenated block copolymer, is used as a thermoplastic rubber layer. If the ethylene copolymer is less than 10 parts by weight, the film formability becomes poor, which is undesirable, whereas if it is greater than 150 parts by weight the film layer prepared from the resin composition lacks rubber elasticity so the object of the present invention cannot be attained.

In the present invention the nonwoven fabrics include polypropylene fibers, acrylic fibers, polyester fibers, polyamide fibers, rayon fibers, acetate fibers, triacetate fibers, polyvinyl alcohol fibers, polyvinyl chloride fibers, polyurethane fibers, etc., which are oriented only in the warp direction or oriented randomly only in the warp direction.

Only nonwoven fabrics with such fiber orientation can manifest stretchability when they are laminated with thermoplastic rubber layers.

In the present invention, the constitution of laminates comprising thermoplastic rubber layers (R) and the nonwoven fabric layers (T) is (R)/(T), (R)/(T)/(R), or (T)/(R)/(T), and its selection is based on the object of the application.

The lamination methods include melt extrusion of a resin composition composed of hydrogenated block copolymer and ethylene copolymer on a nonwoven fabric layer (extrusion laminate method), pasting method using adhesives, etc., however, in view of the excellent gloss, antiblocking, and evenness of films formed, the use of T-die chilled roll method for the manufacture of the films is preferable.

The thickness of the thermoplastic rubber layer is 10-100 μm , preferably 20-50 μm .

If it is less than 10 μm , the mechanical strength is insufficient, napping occurs, and the adhesive property is inferior, thus it is undesirable.

If it is greater than 100 μm , the stretchability is inferior which is undesirable also.

The basis weight of the nonwoven fabrics is 5-500 g/m^2 , preferably 50-200 g/m^2 .

If it is less than 5 g/m^2 , the functions (imparting of tensile strength, breaking property, slipping property, hand, and fine appearance) of the nonwoven fabrics cannot be manifested, whereas if it is greater than 500 g/m^2 the softness, bending resilience, light weight, hand, etc., disappear, which is undesirable. The fineness of the fibers constituting the nonwoven fabrics to be used is 0.1-100 denier, preferably 1-30 denier.

If it is less than 0.1 denier the tensile strength is too weak, whereas if it is greater than 100 denier it lacks softness, light weight, feeling, etc., which is undesirable.

Application Example 1

100 parts by weight styrene-ethylene-butylene-styrene copolymer (Tuftec H-1052, Asahi Chemical Industry Co., Ltd.), 50 parts by weight ethylene-ethyl acrylate copolymer (DPDJ-6169, Nippon Unicar Co., Ltd.) with EA content 18% and $\text{MI} = 6$, 0.1 parts by weight antioxidant (Irganox 1010, Ciba-Geigy Corporation), and 0.3 parts by weight lubricant (stearic acid amide) were kneaded at 160°C for 10 min using a Banbury mixer, followed by pelletizing using a granulator. On the one hand nylon fibers (5 denier, basis weight 60 g/m^2) in which the fibers are oriented only in the warp direction is shown in Figure 1. A nonwoven fabric in which the fibers were oriented parallel only in the warp direction was provided.

Next, on the above-mentioned nonwoven fabric the above-mentioned pellets were extrusion-laminated under the following conditions.

Extruder (65 mm diameter): three-stage screw

T-die: 500 mm width

Air gap: 110 mm

Processing rate: 50 m/min

Thickness of laminate: 20 μm

Resin temperature: 280°C

Then the wound roll was cut properly and the laminate was evaluated.

Adhesive strength between the resin and the nonwoven fabric

The fibers of the nonwoven fabric were not peeled off from the resin, but the fibers which constituted the nonwoven fabric were peeled off from each other.

Stretchability

The stress was 240 kgf/cm^2 when it was stretched 600% in the filling yarn (transverse) direction, but when the tensile stress was removed it returned to its original shape.

It was unable to stretch in the warp direction thus there was no stretchability.

Application Example 2

An experiment identical to that of Application Example 1 was carried out except that instead of using the nonwoven fabric as in Application Example 1 shown in Figure 1, a nonwoven fabric in which the fibers meandering in the warp direction shown in Figure 2 was used.

It was possible to stretch 400% in the filling yarn (transverse) direction and 300% in the warp (longitudinal) direction.

When the tensile stress was removed in both directions it rapidly returned to its original condition.

Application Example 3

An experiment identical to that of Application Example 1 was carried out except that instead of using the ethylene-ethyl acrylate copolymer of Application Example 1, ethylene-vinyl acetate copolymer (VA content 18%, $MI = 10$, NUC-3190, Nippon Unicar Co., Ltd.) was used. The product had a slight acetic acid odor but there was no problem with its properties.

Both the adhesive property and the stretchability were roughly the same as those of Application Example 1, thus it was a practical product.

Application Example 4

An experiment identical to that of Application Example 1 was carried out except that instead of using the ethylene-ethyl acrylate copolymer of Application Example 1, ethylene-zinc methacrylate copolymer (Himilan AM-6004, Mitsui-Du Pont Co.) was used.

The adhesive property and stretchability were roughly the same as those of Application Example 1, thus it was of practical use.

Application Example 5

An experiment identical to that of Application Example 1 was carried out except that 10 parts by weight ethylene-ethyl acrylate copolymer were used.

The drawdown property was slightly poor but it was able to laminate. The stress was 210 kgf/cm^2 when the laminate was stretched 600%, and when the tensile stress was removed it returned very rapidly to its original shape.

Application Example 6

An experiment identical to that of Application Example 1 was carried out except that 150 parts by weight ethylene-ethyl acrylate copolymer were used.

The extrusion coatability was very good, however, the stress was 320 kgf/cm² when the laminate was stretched 300%, and when the tensile stress was removed it did not rapidly return to its original shape, but sufficient stretchability was recognized.

Comparative Example 1

An experiment identical to that of Application Example 1 was carried out except that instead of using the styrene-ethylene-butylene-styrene copolymer of Application Example 1, nonhydrogenated styrene-butadiene-styrene copolymer (Cariflex TR 1101, Shell Kagaku K.K.) was used. The drawdown property was poor at the time of lamination, thus it could not be used for lamination.

From this comparative example it is clear that the hydrogenated copolymer is an essential element of the present invention.

Comparative Example 2

An experiment identical to that of Application Example 1 was carried out except that instead of using the ethylene-ethyl acrylate copolymer of Application Example 1, low-density polyethylene prepared by the high-pressure process (NUC-8008, density 0.918, MI = 5.0, Nippon Unicar Co., Ltd.) was used. There was no problem in the extrusion coatability, but the adhesive property between the resin film and the nonwoven fabric was poor and the stretchability of the laminate was poor, thus it was not practical.

From this comparative example it is clear that the ethylene copolymer is an essential element of the present invention.

Comparative Example 3

An experiment identical to that of Application Example 1 was carried out except that instead of using the nonwoven fabric as in Application Example 1 of Figure 1, a commonly used nonwoven fabric of Figure 3 was used. The thusly prepared laminate was not stretchable in both warp and filling yarn (i.e., longitudinal and transverse) directions and was not practical.

Effect of the invention

The present invention is laminates comprising thermoplastic rubber elastic layers made of hydrogenated block copolymers and ethylene copolymers, and nonwoven fabrics comprising

fibers parallelly or randomly oriented in the warp direction, therefore at the time of manufacture, the extrusion laminating method which enables high-speed mass production can be used, and the thusly manufactured laminates have stretchability, waterproof property, dust-preventing property, gas barrier property, heat-sealable property, softness, and mechanical strength, and they are a novel material and are suitable as base materials for clothing, bandages, supporters, adhesive plasters, diaper covers, packaging materials, industrial materials, etc.

Brief explanation of the figures

Figure 1 shows a rough drawing of a nonwoven fabric comprising fibers parallelly oriented in the warp direction.

Figure 2 shows a rough drawing of a nonwoven fabric comprising fibers randomly oriented in the warp direction.

Figure 3 shows a rough drawing of a commonly used nonwoven fabric comprising intertwined fibers.

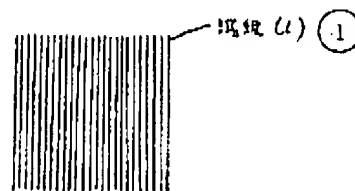


Figure 1

Key: 1 Fiber

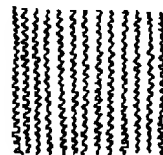


Figure 2



Figure 3